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MECHANISM OF THE NITRATION AND OXIDATION OF CYCLOHEXANE

A.I. Titov and M.K. Matveyeva

From the standpoint of classical organic chemistry, the nitration of cyclohexane with nitric acid was investigated by V.V. Markovnikov (1), Aschan (2), and in more detail by S.S. Nametkin (3). The chief products of the reaction were nitrocyclohexane and adipic acid.

Our theory of nitrating the paraffin chain (4) explained the mechanism of the reaction between cyclohexane and nitric acid, permitted us to establish that nitrogen dioxide is a more effective nitrating and oxidizing agent [than nitric acid], and uncovered a series of other chemical phenomena in this field.

On the basis of our theory, the chemical processes in the nitration of cyclohexane under ordinary conditions may be formulated briefly as follows:

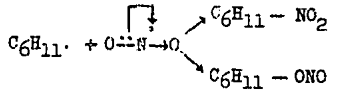
Nitric acid by itself does not react with cyclohexane but serves only as a source for the formation of oxides of nitrogen from lower oxides by the equations:

$$2HNO_3 + NO \rightleftarrows 3NO_2 + H_2O, \quad HNO_3 + HNO_2 \rightleftarrows 2NO_2 + H_2O \qquad (1)$$

Just as with oxides of nitrogen and nitric acid, the first stage of the reaction with cyclohexane is an attack by a monomer of nitrogen dioxide in the form of a radical on the hydrocarbon, leading to the formation of free cyclohexyl; this is shown as follows:

$$C_6H_{11}-H + NO_2 \rightarrow C_6H_{11}\cdots H\cdots NO_2 \rightarrow C_6H_{11}\cdot + HNO_2 \qquad (2)$$

Cyclohexyl immediately reacts with nitrogen dioxide, giving a mixture of the nitro compound and the nitrite, as follows:



$$C_6H_{11}\cdot + O{\cdots}N\rightarrow O \begin{cases} \nearrow C_6H_{11}-NO_2 \\ \searrow C_6H_{11}-ONO \end{cases} \qquad (3)$$

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Under special conditions, the interaction of cyclohexyl with NO, N_2O_4, and HNO_3 can play a significant role.

Nitrocyclohexane, formed by equation (3), is almost entirely preserved in the end products of the reaction. Cyclohexyl nitrite rapidly enters into an equilibrium reaction with water:

$$C_6H_{11}ONO + H_2O \rightleftarrows C_6H_{11}OH + HNO_2 \tag{4}$$

The cyclohexanol that is formed oxidizes quite readily into adipic acid and then is esterified by the latter, i.e., into acid and neutral cyclohexyl adipates; cyclohexyl nitrate is formed in an analogous fashion. In accordance with theory and chemical experiments, esters of cyclohexanol are more stable to the action of oxidizing agents than the free alcohol.

In agreement with these conclusions, we established experimentally that nitric acid, which is free of oxides of nitrogen, does not react, for practical purposes, with cyclohexane under any of the most diverse conditions. The reaction between cyclohexane and nitrogen dioxide takes place to a noticeable extent even at room temperature and is almost completed after 2 months' standing; to carry out the reaction at 100°, one hour of heating is sufficient. The reaction with nitrogen dioxide yields the same products as the one with nitric acid. Heating cyclohexane at 100° with a large excess of nitrogen dioxide can lead to an explosion. This is probably due to the chain reaction $C_6H_{11} + H + NO_2^* \rightarrow C_6H_{11}\cdot$; $C_6H_{11}\cdot + N_2O_4 \rightarrow C_6H_{11}ONO + NO_2^*$ etc. and to the development of subsequent oxidation processes.

Nitration and oxidation of cyclohexane with nitric acid took place only in the presence of nitrogen dioxide, and to an extent proportional to the quantity of the latter. It is interesting that addition of nitric acid, even of a specific gravity of 1.3, to nitrogen dioxide reduced the nitrating and oxidizing activities of nitrogen dioxide.

The explanation of the role of oxides of nitrogen permitted understanding the advantages of the nitration of cyclohexane in sealed tubes by the Konovalov-Nametkin method and led us to a series of new conclusions which were confirmed by experiment. Consideration of the role of diffusion of nitrogen oxides from the hydrocarbon layer into the acid layer and of nitrogen dioxide in the opposite direction led us to the idea of the importance of the dimensions of the interface between the acid and hydrocarbon phases and of the height of the layers to the rate and direction of the reaction. In accordance with this, it developed that the total yield of the reaction when the tubes were placed in a horizontal position was 2-3 times greater than when they were placed in a vertical position, and that the difference between the yields was greatest when the amount of nitrogen dioxide first added was least. The yield of adipic acid, in agreement with theory, increased more than that of the nitro compound; in some experiments, its yield was almost five times greater. The effect of factors of this kind had not been noted by previous investigators; in the literature there are even direct statements in regard to carrying out the nitration by Konovalov's method in vertically placed tubes.

The radical-molecular character of the reaction was additionally confirmed by establishing that the reaction took place in the hydrocarbon and not in the acid phase and by the absence of any accelerating action of additions of protonic and aprotonic acids (H_2SO_4, $AlCl_3$) and mercury salts.

The experimental proof of our hypotheses of the mechanism of formation of oxidation products was begun by clarifying the chemical behavior of the previously unknown cyclohexyl nitrite. It developed that this nitrite decomposed merely on standing into a mixture of cyclohexanol, adipic acid, and the previously undescribed mono and dicyclohexyl adipates, presumably cyclohexanone, dicyclohexyl ether, and esters of lower dicarboxylic acids were also present in the mixture.

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We then succeeded in establishing the formation of cyclohexyl nitrite and the above-mentioned products of its decomposition during the reaction between cyclohexane and nitrogen dioxide under mild conditions produced by heating for one hour in the presence of a large excess of the hydrocarbon. For the qualitative and quantitative determination of cyclohexyl nitrite in the products of the reaction and the separated fractions, its capacity to diazotize sulfanilic acid was utilized. With the aid of this reaction, the formation of nitrites was similarly established in the analogous case with n-pentane, in the reaction between cyclohexane and nitric acid, and finally, in the case when the reaction was carried out in the gaseous phase.

Investigation of the neutral portion of the reaction products of one of the experiments on nitrating cyclohexane with nitrogen dioxides at mild conditions, showed that this portion consists of roughly 50 mol % of nitrocyclohexane, 8% of cyclohexyl nitrite and 8% of cyclohexanol, 20% of adipic acid, and 14% of various esters of cyclohexanol. One fraction contained about 30% of cyclohexyl nitrite and 60% of cyclohexanol, judging from the combined results of diazotization with sulfanilic acid, oxidation under mild conditions into adipic acid, and isolation of cyclohexyl-3,5-dinitrobenzoate (melting point, 112°) resulting from the action of 3,5-dinitrobenzoyl chloride. Dicyclohexyl adipate was isolated in this experiment in the crystalline state from the last fraction obtained by distilling the reaction product freed of the acids.

Except for nitrocyclohexane, which is stable to oxidation, all the other fractions of the neutral part of the reaction products were easily converted to adipic acid with nitric acid. This explains the formation of almost equimolecular quantities of nitrocyclohexane and adipic acid in addition to lower homologues under ordinary, rather severe nitrating conditions. These experimental results also agree with the observed similarity of the composition of acids formed during the oxidation of cyclohexanol with nitric acid (5) on the one hand and the oxidation of cyclohexane (3) on the other hand.

All of these experimental data leave no doubt as to the accuracy of the basic aspects of our theory of nitrating cyclohexane and its applicability to the mechanism of the formation of oxidation products. We also found experimental confirmation of other aspects of our theory. For example, it was found that when the total concentration of nitrogen dioxide is increased, the yield of oxidation products is increased and the yield of nitrocyclohexane is reduced, since the probability of collisions between cyclohexane and dimers of nitrogen dioxide is increased when this happens, leading to the formation of cyclohexyl nitrite only. In nitration experiments with N_2O_4 at 60°, a small quantity of cyclohexyl nitrate was isolated. It had a boiling point of 96 - 98° at 40 mm.

We will give a short description of some of the experiments that clarify the formation mechanism of oxidation products of cyclohexane. (For the remaining experimental data, see (6).)

1. Cyclohexyl nitrite and its spontaneous decomposition. Cyclohexyl nitrite was synthesized from cyclohexanol in the usual manner. It formed a slightly yellowish liquid with a boiling point of 40 - 54°. From 69.8 g of the nitrite, 2.6 g of pure adipic acid were isolated after 60 days of standing. Extraction with a soda solution yielded an additional 0.3 g of the acid and with 5% caustic alkali, nearly 7 g of crude acid, i.e., cyclohexyl adipate were obtained. Distilling the residue at 40 mm yielded the following fractions: I, 53 - 55°, 27.4 g; II, 55 - 77°, 1.4 g; III, 77 - 99°, 5.1 g (cyclohexanol); at 5 mm; IV, 70 - 100°, 6.9 g; V, 130 - 170°, 1.2 g; and VI, 205°, 1.5 g. The last fraction yielded crystals melting at 36° identical with dicyclohexyl adipate obtained synthetically by heating 5 g of adipic acid with 5.2 g of cyclohexanol at 135° for 10 hours (yield of acid, i.e., ester, 3.1 g; neutral ester, 3.5 g).

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2. Evidences of the formation of cyclohexyl nitrite and the products of its decomposition in the nitration of cyclohexane. Eighty milliliters of cyclohexane and 12 ml of nitrogen dioxide were heated for one hour at 100° in four sealed tubes, each having a volume of 90 ml. On cooling, 3.6 g of adipic acid were isolated from the reaction mixture. After acidifying the soda extract, a little more of a mixture of crystalline acids was removed, and with a caustic alkali extraction, an oil having the properties of acid, i.e., cyclohexyl adipate was removed. Distillation of the neutral residue yielded 52 ml of cyclohexane (fraction I), fraction II and III at 40 mm, and the following fractions at 5 mm: II, 45 - 70°, 1.5 g; III, 100 - 110°, 8.5 g; IV, 110 - 140°, 1.7 g; V, 200°, 0.3 g. Fraction II consisted chiefly of cyclohexyl nitrite and cyclohexanol. Of this fraction 0.382 g was mixed with 10 ml of 0.25 N solution of sulfanilic acid; after acidification and agitation for one half hour, 6.4 ml [of a standard solution] were spent on the back titration, which corresponds to 30.4% nitrite. An amount of 0.302 g of the same fraction reacted rapidly with 5 ml HNO_3 of s.g. 1.2. Here, 0.08 g of pure, 0.26 g of crude adipic acid, and 0.07 g of nitrocyclohexane were obtained, which corresponds to 52.4% of cyclohexanol, after allowing for the nitrite; the latter was also isolated as 3,5-dinitrobenzoate of a melting point of 112°. The total content of cyclohexyl nitrite in all the fractions, as determined by the diazo method, was 1 g, or 7% of the spent hydrocarbon.

According to the data on oxidation with nitric acid, fraction III contained about 14% of cyclohexanol and cyclohexyl nitrate and 85% of nitrocyclohexane. Fraction IV consisted chiefly of dicyclohexyl ether. The latter fraction yielded crystals of dicyclohexyl adipate, melting point 36°, identical with the product of known constitution. After nitration under milder conditions, fraction III yielded cyclohexyl nitrate, with a boiling point of 89° at 30 mm, subsequently to removing the nitrocyclohexane with a caustic solution.

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